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Materials Issues in the Development of High Data-Transfer-Rate Phase-Change Compounds

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ABSTRACT

A model is presented to calculate glass-transition temperatures. This model in combination with experimental data is used to evaluate archival-life stability of common phase change materials Ge₂Sb₂Te₅ and doped eutectic Sb₂Te compositions.

On the basis of this model, novel high-data-rate phase change compositions have been identified near and on the pseudo-binary line InSb-GaSb in the ternary system Ga-In-Sb.

INTRODUCTION

Phase-change optical recording has evolved to a mature technology that is applied in re-writable data-storage systems such as CD-RW, DVD+RW and DVD-RAM. In these systems, the recording of information is based on writing and erasing amorphous marks in a crystalline layer of a phase-change material. Besides sufficient optical contrast between the crystalline and amorphous state and a sufficiently low melting point attainable with moderate lasers powers, the crystallisation behaviour at various temperatures is one of the most important aspects in developing phase-change materials. At elevated temperatures the crystallisation time of amorphous marks should be short to enable high data-rate (<100ns). This is because the maximum rate at which previous data can be overwritten with new data (within a single pass of the laser spot) is limited by the rate at which amorphous marks of the previous data can be crystallised. On the other hand, at room temperature the crystallisation rate has to be virtually zero in order to ensure that recorded amorphous marks are stable against spontaneous recrystallisation for 30-50 years (archival-life stability). These two conflicting requirements complicate the development of new phase-change materials for high-speed rewritable discs.

In the first part of the paper, the archival-life stability of phase-change discs is addressed. A model is presented that can be applied to select and improve promising phase-change materials compositions with respect to their amorphous-mark stability. Isothermal crystallisation experiments on recorded amorphous marks have been performed to support the model and to determine the archival life of phase-change discs.

Based on the model, novel compositions of Ga-In-Sb phase-change materials were investigated as possible candidates for high data-rate rewritable optical recording. Dependence of stability and high speed crystallisation of amorphous marks on composition is discussed.

AMORPHOUS MARK STABILITY

The archival life of a phase-change disc is generally determined by the thermal stability of recorded amorphous marks. When the disc is stored at elevated temperatures, the marks may spontaneously re-crystallise, resulting in progressive deterioration of the data. To accelerate

optimisation of phase-change materials a model has been developed [1] that can be used to calculate glass-transition temperatures for phase-change materials of various compositions. These glass-transition temperatures are used to estimate the amorphous-mark stability and the corresponding archival life. The glass-transition temperature represents the temperature above which an amorphous matrix can attain various structural configurations and below which the matrix is frozen into a structure which cannot easily change to another structure. Thus, crystallisation below the glass-transition temperature is extremely slow and a strong correlation between glass-transition temperature and thermal stability of recorded marks is expected.

It is reasonable to assume that the glass-transition temperature must be related to the magnitude of the cohesion forces within the amorphous network since these forces must be overcome to allow atomic movement. Therefore, a promising approach to determine glass-transition temperatures is to find a correlation with atomisation energies of the amorphous network. These energies can be calculated by summing all individual bond energies, taking into account the number of bonds per atom and the energy per bond. The number of bonds per atom is determined by the number of valence electrons of the corresponding atom. For instance, Te has 6 valence electrons and forms 2 bonds, while Ge has 4 valence electrons and forms 4 bonds. In a covalent matrix, metallic-like elements form 4 covalent bonds, but donate additional bonds to their neighbouring chalcogenide atoms (Te, Sb etc.) by transfer of valence electrons. Bond energies can be obtained from the known atomisation energies of stoichiometric compounds [1]. In table 1, bond energies and number of bonds are listed for a selected set of elements.

In the literature many glass-transition temperatures are reported for covalent amorphous materials of various compositions. With the method described above we can calculate the atomisation energy for each composition and relate them to the reported glass transition temperatures. The overall empirical relation found between the glass-transition temperature T_g (in Kelvin) and atomisation energy, E_a , (in kJ/mol) is [1]

$$T_v = 3.44 E_u - 480$$

Using the above model, glass-transition temperatures were calculated for the ternary system Ge-Sb-Te. This system contains the well-known stoichiometric phase-change compounds along the GcTc-Sb₂Te₃ tie-line, i.e. GcTe, Ge₂Sb₂Te₅ and Ge₁Sb₂Te₄. The Ge-Sb-Te system also includes the compound Sb₂Te. This compound forms the basis for the so-called fast-growth materials (FGM) currently applied in media CD-RW and DVD+RW discs. These phase-change materials can be viewed upon as Sb₂Te doped with Sb, In, Ag and/or Ge.

Table I. Bond energies (in kJ/mol) for combinations of selected elements. The number of bonds formed by each element is indicated between brackets.

	Te (2)	Sb (3)	Ge (4)	Ga (4+1)	In (4+1)	Ag (4+3)
Te (2)	197	186	192	152	133	76
Sb (3)	186	175	181	138	120	64
Ge (4)	192	181	186	142	123	69
	152	138	142	90	70	21
In (4+1)	133	120	123	70	50	2
Ga (4+1) In (4+1) Ag (4+3)	76	64	69	21	2	-50

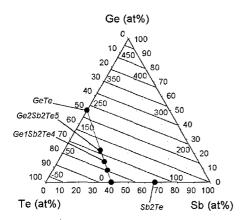


Figure 1. Calculated glass-transition temperatures (in °C) for the system Ge-Sb₂Te. Stoichiometric phase-change compositions on the pseudo-binary line GeTe-Sb₂Te₃ are shown in the plot. The binary compound Sb₂Te is also shown, since current CD-RW and DVD+RW materials are based on doping Sb₂Te with Sb, Ag, In and/or Ge.

Figure 1 shows calculated lines of constant glass-transition temperature for the ternary system Ge-Sb-Te. It is seen that increasing the Ge content is very effective for increasing the glass-transition temperature. This is due to the fact that Ge forms 4 bonds with relatively high bond energy. Also a high Sb/(Sb+Te) ratio is beneficial for a high glass-transition temperature. Assuming that a minimal glass-transition temperature of 100° C is required for sufficient amorphous-mark stability, one sees that the compounds GeTe and Ge₂Sb₂Te₅ fulfil this requirement, while the compounds Ge₁Sb₂Te₄ and Sb₂Te do not. It has been found that phase-change discs based on Ge₁Sb₂Te₄ indeed have insufficient archival-life. The model shows that the amorphous mark stability of Sb₂Te can be increased by alloying. Calculations for (Sb₂Te)_{0.93}Y_{0.07} with Y = Ge, Ag or In yields glass-transition temperatures of 106, 83 and 71°C, respectively, which have to be compared with the value of 76°C for Sb₂Te. Addition of Ge is thus expected to be more effective for increasing the amorphous-mark stability than addition of In and Ag.

A first indication for the archival-life stability of phase-change materials is generally obtained by measuring the crystallisation temperature of the sputter-deposited amorphous state. A more accurate prediction can be obtained by measuring the (low temperature) activation energy for crystallisation of recorded amorphous marks, and by using this value to extrapolate the lifetime of recorded marks at ambient temperatures. Such experiments have been performed for $Ge_2Sb_2Te_5$ and for eutectic Sb_2Te doped with In or Ge.

Figure 2 shows transmission electron microscope (TEM) images which visualise what happens when amorphous marks recorded in doped eutectic Sb_2Te are heated in a furnace. These materials are characterised in that crystallisation proceeds by growth of the crystalline edge towards the mark centre [2], as is clearly seen in the figure. The crystallisation mechanism for stoichiometric $Ge_2Sb_2Te_5$ is completely different. For this material, crystallisation takes place by nucleation of many crystallites in the interior of the mark until the mark is completely filled [2].

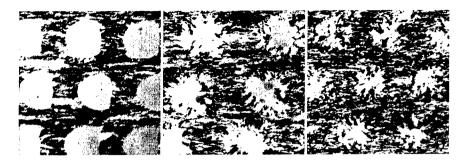


Figure 2. TEM-images of amorphous marks (400nm) recorded under DVD-conditions in a phase change disc based on Ge-doped eutectic Sb₂Te, after recording (left panel), after annealing for 1 hr at 165°C (central panel), and after annealing for 1 hr at 175°C (right panel).

Figure 3 shows the extrapolated archival life as a function of temperature for $Ge_2Sb_2Te_5$ and for the doped eutectic Sb_2Te compositions. The archival life was estimated as 10% of the measured isothermal crystallisation time since partly re-crystallised marks already will deteriorate the read-out significantly. The eutectic materials appear to be more stable than $Ge_2Sb_2Te_5$ at ambient temperature, which is mainly due to the higher activation energy involved. In accordance with the calculated glass transition temperatures, addition of Ge is much more effective than addition of Ge in to increase the amorphous stability of doped eutectic Sb_2Te .

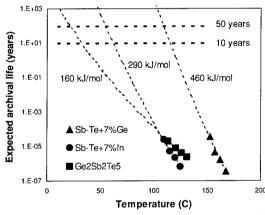


Figure 3. Expected archival life of recorded amorphous marks (DVD conditions). Activation energies are shown in the plot. The activation energy of Ge₂Sb₂Te₅ is remarkably lower than that of the doped Sb-Te materials. This might be related to the different type of crystallisation process involved.

PROPERTIES OF NOVEL PHASE CHANGE MATERIAL: GaInSb

More than 15 years ago, InSb and GaSb were discovered to show extremely fast crystallisation upon laser heating of the amorphous state [3]. At that time, they were basically regarded as write-once materials instead of rewritable materials, because their high crystallisation speed would make it impossible to write amorphous marks in a crystalline layer. Since then, cooling rates of phase-change stacks have improved and also laser drivers have been developed allowing

laser pulses of only nanosecond duration. This has led us to re-investigate these compounds and mixtures thereof for application in high data-rate rewritable recording.

First, we calculated glass-transition temperatures using the model described in this paper. The results are plotted in Figure 4. It is seen that InSb-rich compositions and compositions to the right of the InSb-GaSb tie-line have low glass transition temperatures. The latter compositions only have sufficiently high glass-transition temperature at high Ga/In-ratio.

Static tester experiments [4] were performed to measure the complete erasure time (CET) of written amorphous marks. Five compositions on the InSb-GaSb tie-line were measured. Measured CET-values are plotted in Figure 4. The CET-values were independent of the amorphous mark-size, which is typical for nucleation dominated crystallisation. Short crystallisation times below 25 ns were observed for InSb-GaSb mixtures with more than 25% GaSb. Ultra-short crystallisation times close to 10 ns were observed for GaSb rich compositions. Additional measurements showed that crystallisation times could be decreased even further by using nucleation-promoting cap-layers, or by increasing the thickness of the phase change layer.

In Figure 5 are plotted the expected archival life of InSb, $In_{38}Ga_{12}Sb_{50}$ and $In_{25}Ga_{25}Sb_{50}$ as determined experimentally with the procedure described in the previous section. The expected archival life of the respective compositions at 25°C is 2 days, 1 year and 3000 years. GaSb-rich compositions combine a high crystallisation rate with a high amorphous mark stability. These compositions, however, have 2 drawbacks. First, the laser power required for writing marks is relatively high, due to the gradual increase in melting temperature when going from InSb to GaSb. Second, the optical contrast between amorphous and crystalline state gradually decreases when going from InSb to GaSb.

Recorder experiments under DVD+RW conditions were performed for some compositions. Data could be written and erased at high speed with sufficient modulation using stacks with low crystalline reflection and high amorphous reflection. Important media parameters such as the number of direct overwrite cycles and erasability need to be further optimised.

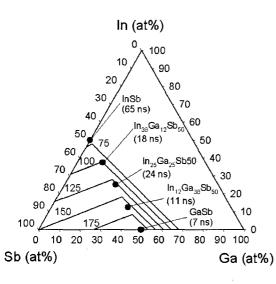


Figure 4. Calculated glass transition temperatures (in °C) for the system Ga-In-Sb. Compositions for which complete erasure times of written amorphous marks have been measured (under DVD conditions) are shown also in the plot together with the corresponding values. Stack design: substrate/ZnS-SiO₂/GaInSb (25 nm)/ ZnS-SiO₂/Al.

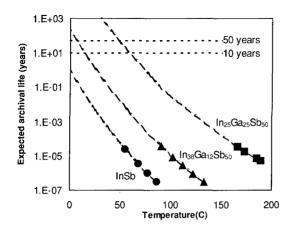


Figure 5. Expected archival life of recorded amorphous marks (DVD conditions) for 3 Ga-In-Sb compositions: InSb, In₁₂Ga₃₈Sb₅₀ and In₂₅Ga₂₅Sb₅₀. Data was measured using the procedure described in the text. The activation energy is approximately 140kJ/mol, which value is close to that determined for Ge₂Sb₂Te₅, for which the crystallisation is also nucleation dominated.

CONCLUSIONS

Phase-change discs based on Ge-doped eutectic Sb₂Te have excellent archival life. As predicted by model calculations, the archival life of In-doped eutectic Sb₂Te is much less. Its value is, however, still sufficient (more than 100 year at 25°C). The estimated archival life of Ge₂Sb₂Te₅ is 10-50 years at room temperature. In the ternary system Ga-In-Sb, novel phase change compositions have been identified which combine short crystallisation time (<25ns) with sufficient stability of recorded amorphous marks (more then 50 year at 25°C).

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